



Degradation of PFOA by hydrogen peroxide and persulfate activated by iron-modified diatomite



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ARTICLE INFO

Article history:

Received 11 November 2015

Received in revised form 25 February 2016

Accepted 29 March 2016

Available online 31 March 2016

Keywords:

Perfluorooctanoic acid

Superoxide radical anions

Persulfate

Hydrogen peroxide

Diatomite

ABSTRACT

Perfluorooctanoic acid (PFOA) is one of the most problematic perfluoroalkyl compounds widely used to make fluoropolymers. The exceptional strength of the carbon–fluorine (C–F) bond in PFOA makes it extremely resistant to oxidative attack even by hydroxyl radicals, resulting in its persistence in the environment. As a result, this study investigated generation of superoxide radical anions to reductively decompose such a highly oxidized chemical, PFOA. Catalyzed hydrogen peroxide (CHP) propagations and activated persulfate systems for generating reductive species such as superoxide radical anions along with oxidizing hydroxyl and sulfate radicals were examined. Improved activation mechanism for hydrogen peroxide and persulfate by using iron-modified diatomite (MD), which favorably leads the reaction to generation of the reductive radicals, was proposed. Three comparative systems were efficient in order of CHP > hydrogen peroxide-activated persulfate > alkaline-activated persulfate at PFOA decomposition of 83%, 69% and 48%, respectively, under given conditions. The heterogeneous system employing MD was also compared with a homogeneous system employing dissolved Fe ions to evaluate the effectiveness of MD. All the results supported that MD has significant catalytic activity for the degradation of PFOA when used to activate hydrogen peroxide and persulfate for the generation of superoxide radical anions. The reductive systems coupled with MD exhibited high decompose efficiency for the most recalcitrant chemical, PFOA and thus high potential for the decomposition of other problematic halogenated compounds.

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1. Introduction

Perfluorooctanoic acid (PFOA) is one of the most well-known perfluoroalkyl compounds (PFACs). PFOA has been widely used in numerous industrial and consumer products [1]. PFOA is considered as an emerging environmental contaminant due to its extreme persistence, toxicity, bio-accumulation, and global distribution [2]. PFOA has been detected in soil, air, and water [3,4]. The United States Environmental Protection Agency (USEPA) has classified PFOA as a likely carcinogen [5]. USEPA and many industrial companies are committed to significantly reduce global facility emissions and product content of PFOA and associated chemicals [6]. The

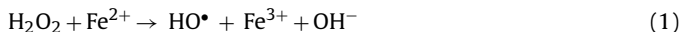
exceptional strength of the carbon–fluorine (C–F) bond and low vapor pressure of PFACs make them extremely resistant to conventional water treatment technologies [7]. The C–F bond is known to be the strongest in organic chemistry [8].

Advanced oxidation processes (AOPs) for the generation of highly reactive oxidizing species such as sulfate radicals (SRs, $\text{SO}_4^{\cdot-}$, $E^\circ = 2.6 \text{ V}$) and hydroxyl radicals (HRs, OH^\cdot , $E^\circ = 2.7 \text{ V}$) have been used to effectively degrade many recalcitrant organic contaminants in water and soil [9]. However, halogenated chemicals are resistant to oxidation as compared to their alkyl analogs because halogenation reduces headgroup electron density [10]. Traditionally, hydrogen peroxide (HP, H_2O_2) has been coupled with ferrous iron (Fe^{2+}) to maximize the production of HRs, so-called Fenton reaction (Eq. (1)) (i.e., minimizing the generation of other less reactive species) [11,12]. In spite of the high reactivity of HRs with

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many organic pollutants, they are known to be much less reactive (virtually non-reactive) with PFOA [13].



Due to the high resistance of PFOA, very high and exogenous energies have been needed in AOPs to initiate and accelerate the decomposition of PFOA [7]. The most researched processes include H_2O_2 /UV photo-Fenton, TiO_2 /UV photocatalysis, and sonochemical processes for HRs generation, and persulfate/UV, peroxymonosulfate/UV, and persulfate/microwave for SRs generation [14–18]. However, these technologies commonly require UV, ultrasound, or microwave radiation, and other working mechanisms than the radicals-based oxidation are also involved in the decomposition processes. These processes are energy-intensive and very expensive, and thus they are not practical for full scale applications [13].

For highly oxidized chemicals such as PFOA, reductive decomposition pathways might be preferred over oxidative decomposition pathways [11]. Superoxide radical anions (SRAs, $\text{O}_2^{\bullet-}$, $E^\circ = -0.33 \text{ V}$) have been used for in situ chemical reduction to reductively decompose highly oxidized compounds [19]. Successful progress of the chemical reduction, which can occur during injection of chemical oxidants, depends on system conditions such as type and concentration of oxidants and pH of reaction environment. SRAs are known to be reactive with halogenated organic compounds such as carbon tetrachloride, trichloroethylene, perchloroethylene, polychlorinated biphenyls, and PFOA [19–21].

In this study, three major pathways to generate SRAs for PFOA degradation were investigated; (i) $\text{S}_2\text{O}_8^{2-}$ (persulfate, PS) under highly alkaline conditions ($\text{pH} > 11$), so-called alkaline-activated PS [20], (ii) $\text{S}_2\text{O}_8^{2-}$ activated by H_2O_2 , so-called HP-activated PS [22], and (iii) H_2O_2 at high concentrations coupled with Fe to initiate a series of propagation reactions, so-called catalyzed hydrogen peroxide (CHP) [23–25]. A heterogeneous system was also chosen for the generation of SRAs due to its many advantages. In some applications such as environmental remediation, a solid support can be easily removed from reaction systems, allowing enhanced recovery of a catalytic material attached to the support from the treated stream [26–29]. Furman and co-workers also showed that the reactivity of SRAs increased linearly with increase in the surface area of a solid material [20,26]. In these HP and PS systems, iron can also be immobilized within the interlayer spatial structure of a solid support to effectively generate various radicals [30].

This present study focused on the decomposition of PFOA by using HP and PS coupled with iron-modified diatomite (MD) as a new heterogeneous activation material. Diatomite ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) is a fine granulated siliceous sedimentary rock, mainly composed of diatom shells and partially other sediments such as clay and quartz [31,32]. Diatomite was chosen as a support material for Fe catalyst due to its low cost, abundance in nature, and advantageous physical properties (e.g., high porosity, high permeability, low thermal conductivity, and chemical inertness) [33,34]. In this work, diatomite was believed to uniformly distribute Fe ions onto its surface and thus to provide more catalytic sites in contact with organic contaminants in water, resulting in enhanced decomposition of PFOA. Consequently, the objective of this study was to evaluate the effectiveness of MD as a new catalyst for the activation of HP and PS and to compare the performance of the three different generation pathways of SRAs for the decomposition of PFOA.

2. Experimental

2.1. Chemicals

PFOA and diatomite were obtained as salts from Sigma-Aldrich and BF-Clay Especialidades Ltd., respectively. Sodium persulfate

($\text{Na}_2\text{S}_2\text{O}_8$, PS) salt, hydrogen peroxide (H_2O_2 , HP) solution, and other chemicals and reagents including iron (II) sulfate heptahydrate salt, iron (III) sulfate salt, sodium hydroxide solution, boric acid, sulfuric acid, and HPLC grade acetonitrile, were obtained from Sigma-Aldrich. All chemicals were used as received. All solutions were prepared in high-purity water.

2.2. Synthesis and characterization of diatomite

MD was prepared by slowly adding 100 g of diatomite into 112 mL of an aqueous mixture of ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) at concentration of 366 g/L and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) at concentration of 183 g/L in an intensively stirred reactor to obtain a uniform slurry. In every 15 min, 55 mL of NaOH solution at concentration of 5 mol/L was added to the slurry and the procedure was repeated four times. The resulting mixture was homogenized for 1 h. Fe-modified diatomite (MD) was recovered and washed via vacuum filtration, oven-dried at 60°C for 24 h, crushed with a mortar and pestle, sieved with a 140 mesh, and stored in a glass vial.

Characterization of the diatomite before and after modification was carried out using established methods. Powder X-ray diffraction (XRD) pattern was monitored using a Siemens/Brucker D5000 XRD unit with Cu K-alpha radiation (40 kV and 40 mA). The diffractogram was recorded in $3\text{--}65^\circ$ 2-theta range with a 0.02 step size and collection time of 1 s per step. X-ray fluorescence (XRF) spectrometry was performed using a Philips PW 2400 XRF spectrometer. Particle size was determined by laser scattering technique on Malvern Mastersize 2000. For scanning electron microscopy (SEM) analysis, diatomite was scanned with LEO 440I SEM. For the SEM analysis, samples were coated with a thin layer of gold.

2.3. Batch experiments

Oxidants used were PS and HP. Radicals including SRAs, HRs, and SRs were generated by the activation of PS and HP with Fe species present in the surface of MD. Initial concentration of PFOA was at 10 mg/L (0.024 mmol/L) in 60 mL of solution. Control experiments were performed with PFOA only (control), PFOA and MD at 1.5 g (control MD), PFOA and HP at 1.5 mol/L (control HP), and PFOA and PS at 0.3 mol/L (control PS). All the experiments were conducted in a 250 mL batch reactor at ambient temperature of 25°C . Reaction solutions were continuously agitated using a magnetic stir bar. To evaluate the effectiveness of the heterogeneous MD system, traditional activation methods for the oxidants to produce radicals were also examined in a homogeneous system by adding the same concentration of Fe ions which was used in the MD system. It should be noted that NaOH used in the preparation of MD caused immediate increase in pH wherever MD was used. All the experiments were conducted in duplicates and the results showed that the experimental errors were less than 5%.

2.3.1. Alkaline-activated persulfate reactions

To study PFOA decomposition by PS, preliminary tests were carried out using PS at two different concentrations of 0.2 mol/L and 0.3 mol/L, 1.5 g of MD, and pH 9 (no pH adjustment was used). Then, the effect of pH was studied at 0.3 mol/L of PS, 1.5 g of MD, and different pH values of 3, 9, and 12. H_2SO_4 and NaOH were used for pH adjustments. For the generation of SRAs and thus the decomposition of PFOA, alkaline-activated PS systems at pH 12 were further investigated with 0.3 mol/L of PS in the presence of 7.5 mmol/L of ferrous sulfate heptahydrate (homogeneous activation) and in the presence of 0.5 g of MD (heterogeneous activation), along with 0.3 mol/L of PS alone (control) [20].

2.3.2. Hydrogen peroxide-activated persulfate reactions

HP is also known to activate PS for the generation of SRAs [22]. Experiments were carried out using 0.5 mol/L of HP and 0.3 mol/L of PS together. Three different conditions were made to evaluate the effectiveness of the system: HP + PS at pH 5, HP + PS + 0.25 g MD at pH 9, and HP + PS + 0.5 g MD at pH 9. No pH adjustments were used.

2.3.3. Catalyzed hydrogen peroxide reactions

For homogeneous CHP reactions to generate SRAs, activation of 1 mol/L of HP with Fe ions was studied by using 7.5 mmol/L of ferrous sulfate heptahydrate and pH of reaction solution was at around pH 5 (no pH adjustment). To investigate the effectiveness of MD containing Fe species to heterogeneously activate HP for generation of SRAs, a comparative experiment was done with 1 mol/L of HP and 0.5 g of MD at pH 9. The experiment employing MD and HP was repeated at pH 9 with different HP concentrations at 0.5, 1, 1.5, and 2 mol/L and different MD doses at 0.5, 1, 1.5, and 2.5 g.

2.4. Extraction and analytical methods

Disappearance of aqueous phase PFOA was monitored with a high performance liquid chromatography (HPLC, 1200 series, Agilent) with suppressed conductivity detector. Bond Elut C18 solid phase extraction (SPE) cartridges (Agilent) were preconditioned with 10 mL of methanol, stabilized with 5 mL of high purity water, loaded with 3 mL of samples, rinsed with 10 mL of high purity water, and then eluted by 1 mL of methanol. Elute from SPE cartridge was analyzed using the HPLC equipped with a quaternary pump and a Venusil AQ C18 column (Agela Technologies). Sample elution was done via a gradient flow of a mixture of water, acetonitrile, and a solution of 9 mM of NaOH and 100 mM of H_3BO_3 at a flow rate of 0.61 mL/min over a period of 15 min with a post-run time of 4 min. Ion suppression was done by an AMMS-300 Anion MicroMembrane suppressor (DIONEX/Thermo). The conductivity signal was collected by a CDD-10AVP conductivity detector (Shimadzu Scientific) and transmitted to Chemstation 35900E A/D interface (Agilent).

3. Results and discussions

Since specific radicals generated in each system over pH conditions have been well reported, less attention was given to identification of such radicals including HRs, SRs, and SRAs [20–26]. Rather, a focus was made to evaluate the effectiveness of MD for the decomposition of the most problematic PFOA and to compare the three major pathways for the generation of SRAs.

3.1. Characteristics of modified diatomite

Table 1 shows XRF analysis result. Fe content in the raw diatomite at 4.79% significantly increased to 17.6% after Fe impregnation. The increased Fe content in MD was expected to greatly influence the heterogeneous activation of HP and PS for the decomposition of PFOA. Decrease in SiO_2 content occurred due to its partial dissolution by NaOH added during the synthesis of MD. Average particle size of the raw diatomite at 29 μm increased to 65 μm after Fe impregnation because Fe oxides and/or hydroxides were deposited onto the surface of the diatomite and the diatomite particles were also agglomerated during Fe impregnation. SEM analysis was used to visually inspect the structure of the diatomite. As shown in Fig. 1(a), the raw diatomite shows cylindrical structures with well-developed porous structure and large void volume. It is mainly disk-shaped and partially pinnate- and platy-shaped. The original geometry of the diatomite was partially transformed after Fe impregnation, as shown in Fig. 2(b). The similar changes of

Table 1

Composition of diatomite before and after modification.

Compound	Raw (%)	Modified (%)
SiO_2	63.71	41.73
Fe_2O_3	4.79	17.60
Al_2O_3	12.54	8.80
Na_2O	1.31	13.39
TiO_2	0.56	1.00
MnO	0.09	0.63
MgO	2.84	2.56
CaO	3.53	2.87
K_2O	1.13	1.31
P_2O_5	0.32	0.75
(LOI ^a)	9.18	9.36

^a Loss by ignition.

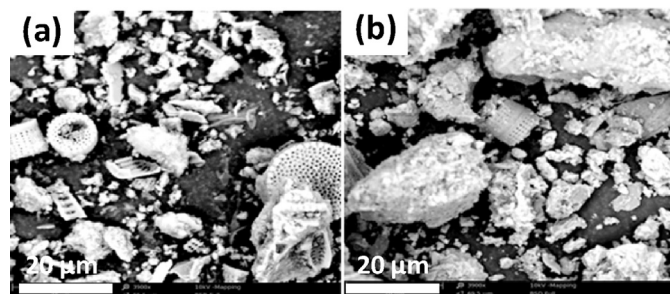


Fig. 1. Scanning electron microscopic images of (a) raw diatomite and (b) modified diatomite.

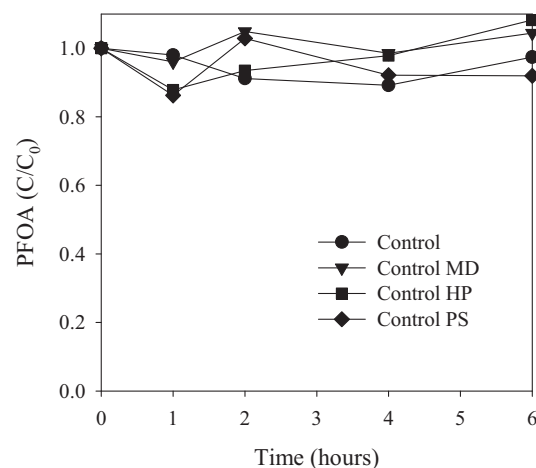


Fig. 2. Decomposition of PFOA by various control systems: control (PFOA only); control MD (PFOA and MD at 1.5 g); control HP (PFOA and HP at 1.5 mol/L); and control PS (PFOA and PS at 0.3 mol/L). PFOA was at 10 mg/L (0.024 mmol/L) in 60 mL of solution.

the diatomite structure were observed elsewhere [34–36]. The surface of MD was covered with layers of Fe oxides and hydroxides. It is believed that the Fe layers are responsible for the activation of HP and PS and the porous structure of the diatomite provides plenty of catalytically active sites for PFOA decomposition.

3.2. Control reactions

Fig. 2 shows control experiment results. As expected, PFOA was stable over time. Either HP or PS alone was not able to decompose PFOA at all, implying that conventional chemical oxidation is not effective to decompose such a recalcitrant chemical. There was also no removal of PFOA in the presence of MD, indicating that MD itself did not either adsorb or decompose PFOA significantly. Negligible

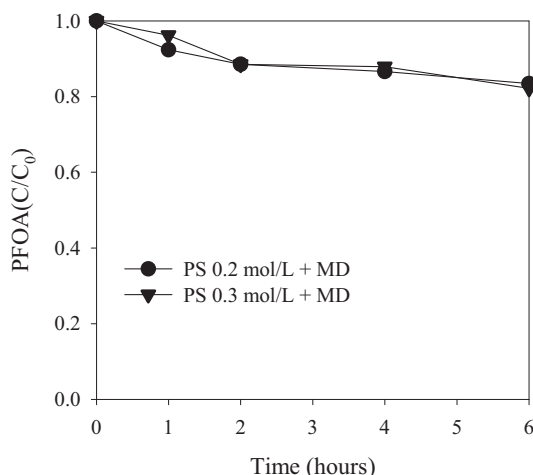


Fig. 3. Decomposition of PFOA by PS+MD system at pH 9 (PS at 0.2 mol/L and 0.3 mol/L and MD at 1.5 g). PFOA was at 10 mg/L (0.024 mmol/L) in 60 mL of solution.

adsorption of PFOA onto MD makes it easier to interpret removal of PFOA in later experiments.

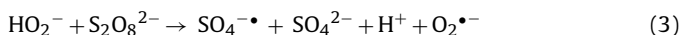
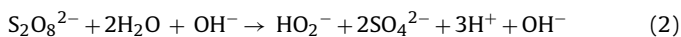
3.3. Persulfate system

3.3.1. Preliminary experiments

Fig. 3 shows decomposition of PFOA by combination of PS and MD at pH 9. The activation of PS by MD resulted in slight decomposition of PFOA. No significant decomposition was found even after 8 days (the result is not shown in the figure). It is well known that PS can be activated by transition metals, Fe in this case, to generate mostly SRs [8]. The low decomposition kinetics of PFOA in this system might be explained solely by incapability of SRs as strong oxidizing species to decompose highly oxidized PFOA [10,13]. Slow kinetics for the generation of SRs via the heterogeneous reaction pathway might also explain the low decomposition kinetics of PFOA. However, the effect can be excluded because even a homogeneous reaction pathway (note Fig. 5 later) also did not show significant reactivity towards PFOA. The applied conditions, which are favorable for generation of mostly SRs, were not successful for PFOA decomposition, which is in agreement with the defluorination rates of PFOA and related chemicals were slow under such oxidative conditions [37].

3.3.2. Effect of pH and alkaline-activated persulfate system

Based on the results shown in Fig. 3, further experiments were conducted to investigate the effect of pH on the generation of SRAs and subsequent reactivity with PFOA. Tests were conducted with PS + MD system (0.3 mol/L of PS and 1.5 g of MD) at pH 3, 9 and 12, as shown in Fig. 4. As expected, no significant PFOA decomposition was observed at pH 3 and 9, similarly to Fig. 3. The pH conditions are known to be favorable for generation of SRs which do not react with PFOA efficiently [10,13]. However, at pH 12, around 50% removal of PFOA was observed after 6 h. Studies reported that decomposition of PS under highly alkaline condition ($\text{pH} > 11$) effectively generates SRAs, along with SRs (Eqs. (2) and (3)) [20]. As a result, the enhanced PFOA decomposition was attributed to exclusively SRAs generated from PS + MD system at such a high pH (Eqs. (2) and (3)) (i.e., alkaline-activated PS system).



In order to further investigate the role of MD in the alkaline-activated PS system, control experiments were conducted without

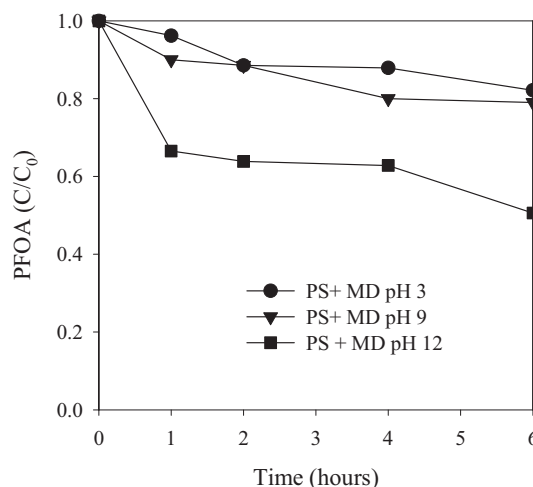


Fig. 4. Decomposition of PFOA by PS+MD system at different pHs of 3, 9, and 12 (PS at 0.3 mol/L and MD at 1.5 g). PFOA was at 10 mg/L (0.024 mmol/L) in 60 mL of solution.

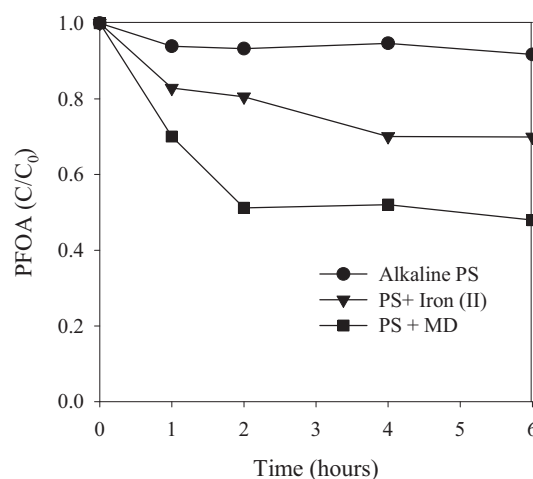


Fig. 5. Decomposition of PFOA by different alkaline-activated PS systems at pH 12: PS at 0.3 mol/L (alkaline PS); PS at 0.3 mol/L and Fe^{2+} ions at 7.5 mmol/L (PS + Iron(II)); and PS at 0.3 mol/L and MD at 0.5 g (PS + MD). PFOA was at 10 mg/L (0.024 mmol/L) in 60 mL of solution.

MD, as shown in Fig. 5. PS alone at pH 12 to produce SRAs and SRs was not so effective. Homogenous generation of SRAs and SRs by PS with dissolved Fe^{2+} ions at pH 12 for the decomposition of PFOA was not as effective as their heterogeneous generation by PS with MD. The result confirms the low reactivity of SRAs in homogenous aqueous systems [26]. MD as a substrate with high surface area for Fe species and PFOA molecules was concluded to have significant influence on PFOA decomposition (Fig. 5) ().

3.3.3. Hydrogen peroxide-activated persulfate system

HP has been widely used to activate PS for remediation of contaminated groundwater and soil [38]. Recent studies proposed that the HP-activated PS system can generate SRAs [22]. However, the reaction mechanism has not been clear yet. As shown in Fig. 6, the HP-activated PS system combined with MD was investigated for the decomposition of PFOA. [22]. Individual oxidant HP or PS did not show any reactivity with PFOA (note Fig. 2) while the HP-activated PS system alone without MD resulted in around 30% decomposition of PFOA after 6 h due to the generation of SRAs [22]. Significantly enhanced decomposition of PFOA was also achieved at 58% and 69% after 6 h in the presence of 0.25 g of MD and 0.5 g of MD, respec-

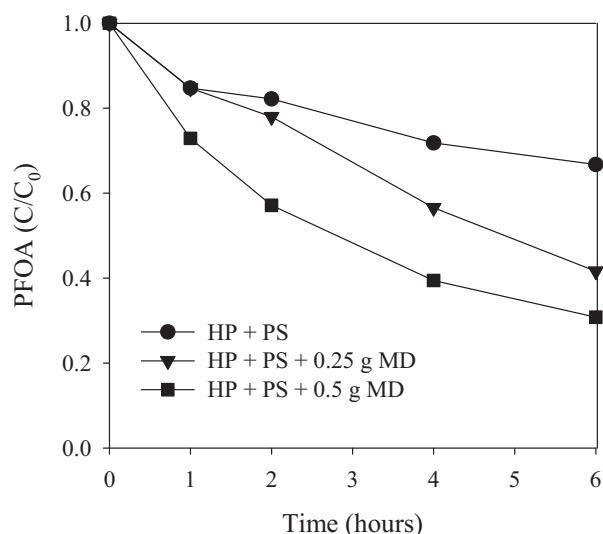
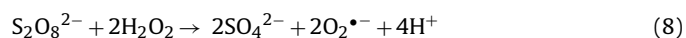
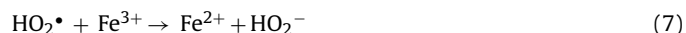
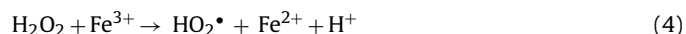


Fig. 6. Decomposition of PFOA by different HP-activated PS systems: HP at 0.5 mol/L and PS at 0.3 mol/L at pH 5 (HP + PS); HP at 0.5 mol/L, PS at 0.3 mol/L, and MD at 0.25 g at pH 9 (HP + PS + 0.25 g MD); and HP at 0.5 mol/L, PS at 0.3 mol/L, and 0.5 g of MD at pH 9 (HP + PS + 0.5 g MD). PFOA was at 10 mg/L (0.024 mmol/L) in 60 mL of solution.

tively. In the presence of Fe species in MD, the reaction mechanisms are more or less complex. The formation of SRAs may occur via the generation of HO_2^- by the activation of HP with Fe ions (Eqs. (4)–(7)). Generated HO_2^- further reacts with PS to form SRAs and SRs (Eq. (3)) [22]. The overall reaction is shown in Eq. (8) where a mixture of HP and PS eventually generates SRAs. Adding more MD containing Fe improved the decomposition of PFOA due to increase in Fe dosage to the system. However, an optimum MD dosage should be determined in a subsequent study because an excessive amount of Fe as a catalyst in MD has been reported to cause radical scavenging effects [39].



3.4. Hydrogen peroxide system

3.4.1. Diatomite-activated hydrogen peroxide system

In previous studies including this present study, SRAs have been shown to effectively degrade highly oxidized compounds, such as PFOA [13]. In the traditional Fenton process employing low concentrations of HP, HRs are dominantly produced (Eq. (1)). However, recent studies have shown that high concentrations of HP (>0.3 mol/L) in the presence of Fe ions also have high potential to produce reductive species such as SRAs along with HRs and HO_2^- via CHP propagation reactions (Eqs. (1),(5)–(7)) [16,18–20]. HRs generated from HP in the presence of Fe ions (Eq. (1)) further react with HP (Eq. (5)) eventually to produce SRAs (Eq. (6)). The generation rates of HO_2^\bullet , SRAs, and HO_2^- become significantly greater at higher HP concentrations, as explained in previous studies [11,40].

Fig. 7 shows generation of SRAs and thus PFOA decomposition by HP in the presence of dissolved Fe ions (i.e., homogeneous system) in comparison to in the presence of MD containing Fe species (i.e., heterogeneous system). Both systems were highly reactive for the decomposition of PFOA. The heterogeneous system employing MD was slightly more efficient than the homogeneous system, as consistently observed in the previous sections. The result supports

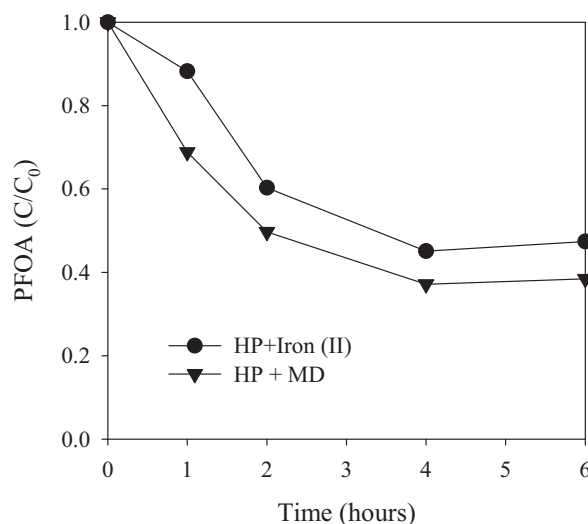


Fig. 7. Decomposition of PFOA by CHP propagation reactions in the presence of dissolved Fe ions (i.e., homogeneous system) and in the presence of MD containing Fe species (i.e., heterogeneous system): HP at 1 mol/L and Fe^{2+} ions at 7.5 mmol/L at pH 5 (HP + Iron(II)); and HP at 1 mol/L and MD at 0.5 g at pH 9 (HP + MD). PFOA was at 10 mg/L (0.024 mmol/L) in 60 mL of solution.

the high catalytic activity of MD as a substrate for immobilizing Fe and the effectiveness of the heterogeneous system for the decomposition of PFOA by SRAs. This finding is in agreement with the conclusions made by Furman et al. that the interaction of solid surface with SRAs increases overall reactivity and thus a linear relationship between the reactivity of SRAs and the surface area of a solid catalyst in aqueous solution is present [26]. The presence of solid surfaces would also enhance the reactivity of SRAs in water, possibly by altering the superoxide solvation shell. Similar phenomenon was observed with an immobilized cobalt catalyst for the decomposition of 2,4-dichlorophenol [41].

3.4.2. Effect of hydrogen peroxide concentration

Optimizing oxidant concentration and catalyst dose is important to effectively decompose organic contaminants because higher concentration and dose do not necessarily grantee better performance of a catalytic system [38,42]. Since the MD-activated HP system was promising, the effect of HP concentration in a range of 0.5–2.0 mol/L with 0.5 g of MD on PFOA decomposition was investigated, as shown in Fig. 8. During CHP reactions, various reactive radical species are generated, including HO_2^\bullet (perhydroxyl radicals as a weak oxidant) and HO_2^- (hydroperoxide anions as a strong nucleophile), along with SRAs (a reductant and nucleophile) and HRs (a strong oxidant) (Eqs. (4)–(7)) [23,24]. Formation of SRAs as strong reducing species depends on reaction pH (note Eq. (6), $pK_a = 4.8$) and HP concentration in the CHP system [18,25]. In general, higher HP concentrations resulted in more PFOA decomposition at 53–66% after 6 h. However, the difference was not significant. The result is in agreement with the recent finding that threshold concentration of HP to generate SRAs (while suppressing formation of HRs) is at around 0.4 mol/L, and thus the performance of the system can be significantly enhanced at the point [17,18–20,23,24]. Excessive amount of HP above the threshold concentration in the reaction medium seemed to favor self-decomposition and to act as a hydroxyl radical scavenger (Eq. (5)), generating other radicals such as SRAs as suggested by Parra et al. [43]. As a result, those tested concentrations at all above 0.4 mol/L did not make any significant difference. Around 0.5–1.0 mol/L was considered as an optimal HP concentration under the specific experimental condition.

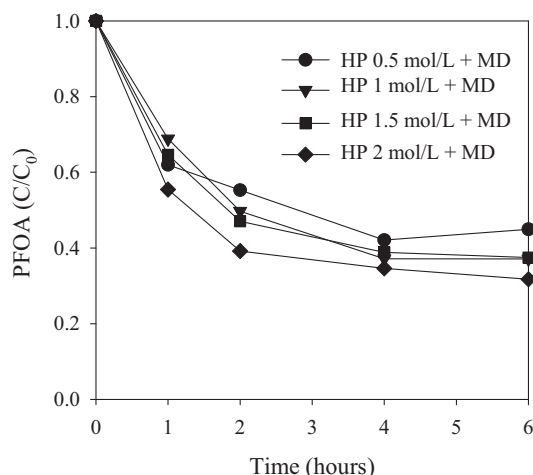


Fig. 8. Decomposition of PFOA by CHP propagation reactions in the presence of MD at 0.5 g under different HP concentrations at 0.5–2.0 mol/L and pH 9. PFOA was at 10 mg/L (0.024 mmol/L) in 60 mL of solution.

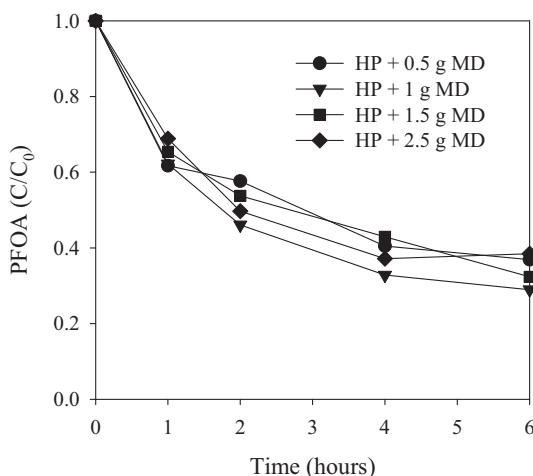


Fig. 9. Decomposition of PFOA by CHP propagation reactions in the presence of HP at 1 mol/L under different MD doses at 0.5–2.5 g and pH 9. PFOA was at 10 mg/L (0.024 mmol/L) in 60 mL of solution.

3.4.3. Effect of modified diatomite dose

The effect of MD dose in a range of 0.5–2.5 g on PFOA decomposition was investigated at 1.0 mol/L of HP, as shown in Fig. 9. Increase in MD dose did not end up with increase in PFOA decomposition. Rather, difference in the performance was marginal. Around 71%, 68%, 64% and 63% of PFOA decomposition was achieved with 1 g, 1.5 g, 2.5 g and 0.5 g of MD, respectively after 6 h. It is generally known that an excessive amount of catalysts (i.e., Fe species impregnated into diatomite in this study) would be detrimental to catalytic decomposition of organic contaminants because excessive metal ions tend to act as scavengers of radical species in some cases [38,39]. Under the specific condition, 0.5–1.0 g of MD was proposed to be an optimal MD dose for PFOA decomposition. The optimum MD dose at 1 g was further confirmed by an experiment employing doubled concentration of HP at 2 mol/L, as shown in Fig. 10. At the increased HP concentration, 1 g of MD still showed higher PFOA decomposition than 2.5 g of MD. The result suggested that the molar ratio of HP to Fe at 40:1 produces SRAs and decomposes PFOA more efficiently.

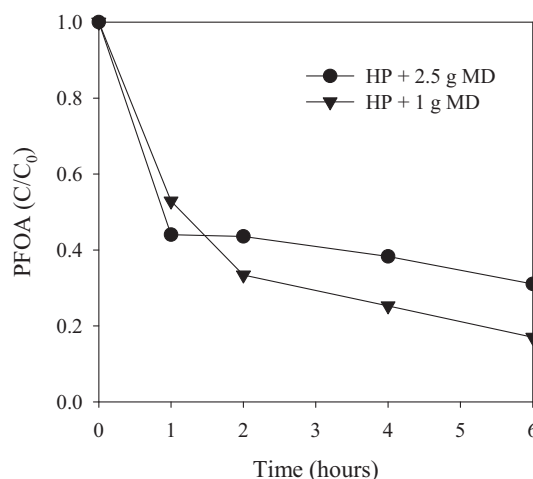


Fig. 10. Decomposition of PFOA by CHP propagation reactions in the presence of HP at 2 mol/L under different MD doses at 1.0 g and 2.5 g and pH 9. PFOA was at 10 mg/L (0.024 mmol/L) in 60 mL of solution.

4. Conclusions

This study was to decompose the most recalcitrant PFOA as one of representative PFACs by using chemical oxidation and reduction. The exceptional strength of the C–F bond in PFOA made it extremely resistant to oxidative attack by HRs and SRs. This study showed the effectiveness of the systems employing SRAs to reductively decompose such a highly oxidized chemical, PFOA. Fe-modified diatomite had significant catalytic activity for the degradation of PFOA when used to activate HP and PS. Improved activation mechanism for HP and PS by using MD, which favorably leads the reaction to generation of SRAs, was proposed. Three comparative systems producing SRAs were efficient for the decomposition of PFOA in order of CHP > HP-activated PS > alkaline-activated PS. Since few previous studies exhibited successful decomposition of the most problematic chemical PFOA, this study showing the effectiveness of the reductive systems coupled with MD for the decomposition of PFOA would be significant. The MD system has high potential for the decomposition of other recalcitrant halogenated compounds. Compared to the most researched AOPs commonly requiring UV, ultrasound, or microwave radiation for the decomposition of PFOA, the proposed chemical process on MD in this study might be practical for full scale applications. For practical applications, MD can be used as a filling material in a permeable reactive barrier coupled with injection of oxidants to treat groundwater contaminated with many recalcitrant chemicals by selectively generating SRAs, HRs, and/or SRs. Once optimized later, comparison between the proposed approach and the most researched AOPs should be given with respect to cost saving and energy requirement.

Acknowledgements

This research was supported partly by the faculty startup funds of The University of Texas at Arlington, the Brazilian Program of Sciences Without Borders, and Agency CAPES (Process # 1944-13-4). This paper has not been subjected to internal policy review of the U.S. EPA. Therefore, the research results do not necessarily reflect the views of the agency.

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